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DAVID SARNOFF RESEARCH CENTER

THIRTEENTH

INTERIM REPORT

INFRARED PHOTOCONDUCTORS

N6onr-23603

January 15, 1953 - April 15, 1953

SECURITY INFORMATION

AD

RADIO CORPORATION OF AMERICA
RCA LABORATORIES DIVISION
PRINCETON, N. J.

June 19, 1953

THIRTEENTH

INTERIM REPORT

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I. Introduction

The main concern of this report is with the photoconductive behavior observed during this period for gold doped germanium. The dark conductivity versus inverse absolute temperature curve for gold doped germanium exhibited a slope of 0.15 ev. which would correspond to a photoionization threshold at about 8 microns. The photoconductivity of gold doped germanium samples was measured at low temperatures and exhibited a broad impurity band extending to 10 microns. The most promising result, however, was that this impurity response from 2 to 10 microns was well above noise with the sample cooled only to liquid nitrogen temperatures. Successful attempts were made in using this sample at liquid nitrogen temperatures to detect objects slightly above ambient room temperature.

II. Properties of Gold Doped Germanium

Temperature Dependence of Conductivity

The samples of gold doped germanium which exhibited the properties outined in the Introduction were cut from a section of crystal grown by drawing from a melt. This material had a resistivity of approximately 10 ohm cm. The two wafers, AA176 and AA177, used in measurements of the temperature dependence of conductivity were taken immediately adjacent to the portion of the crystal from which bars for spectral response measurements were cut.

Both wafers showed, within experimental error, the same temperature dependence of dark conductivity in two runs in the Collins Cryostat. Upon cooling from room temperature, the conductivity first rose slightly to a maximum at about 250°K and then dropped rapidly. Below about 130°K, the dependence of conductivity upon inverse absolute temperature was exponential over the entire range which could be measured. At about 60°K, the dark conductivity was approximately 10^{-10} (ohm cm)$^{-1}$. Leakage currents in the external circuit prevented dark conductivity measurements at lower temperatures. Data for one of the wafers measured are plotted in Fig. 1.

The slope of the exponential portion of the curve is 0.15 ev. If it be assumed that this slope represents the thermal ionization energy of the impurities present and if the thermal

and optical ionization energies are equal, then these samples should exhibit impurity photoconductivity with a long wavelength threshold at 8.3 microns for cell temperatures within the range of easily obtainable coolants, e.g., liquid nitrogen. The spectral response measurements described below demonstrate that this is, in fact, observed. All previously investigated germanium samples require cooling to at least liquid hydrogen temperatures for the development of significant impurity photoconductivity.

The dependence of impurity photoconductive response upon temperature was determined in the Collins Cryostat, over the range from 70°K to 4°K, for the two wafers. The response, excited by radiation from the upper portion of the cryostat at approximately room temperature, rises as the cell temperature is lowered; passes through a maximum at about 50°K; then drops to a minimum at approximately 25°K and finally rises again as the cell temperature is lowered still further. The results are illustrated in Fig. 2. The small absolute magnitude of the photoresponse is due, in part, to the small fraction of the photons from the 300°K source which have wavelengths shorter than the photoconductive threshold of the material and probably, in part, to the non-optimal concentration of impurity in the samples.

One other gold doped germanium sample, AA173, from a different crystal had been measured previously and showed a

considerably different behavior. The principal difference between this sample and AA176 and 177 is the difference in the magnitude of the impurity slope which was 0.05 ev. for AA173. The circumstances of preparation of the two crystals involved were such that the crystal from which AA176 and 177 were cut may have contained a larger concentration of foreign impurity (other than gold) than did the crystal from which AA173 was cut. The difference in behavior observed is consistent with the hypothesis, discussed in another section of this report, that for a multiple valence impurity such as gold a comparable concentration of another impurity which by itself produces the opposite conductivity type may be necessary in order that the valence state having the largest ionization energy be the dominant one.

III. Spectral Response of Gold Doped Germanium

The spectral response of gold doped germanium sample AA178 is shown in Fig. 3. This sample was in the form of a bar 50x130x620 mils. The end of the sample was soldered directly to the base of the copper inner chamber of pyrex double dewar #1. The radiation from the Leiss Monochromator was incident on the lower part of the 130x620 mil face. Measurements of the signal at 25 cps were made with the exit slit width of the Leiss varied from about 1 mm at 10 μmicrons to 0.01 mm at 1.5 micron such that the signal from the thermocouple was the same at all wavelengths. The sample was not directly at the focus of the beam so that it was believed that changing the slit width did not materially affect the size of the illuminated area.

At room temperature (300°K) only the normal intrinsic response and threshold was observed. On cooling to dry ice temperature (195°K), response beyond the intrinsic threshold out to 4 microns was measured. Reference to Fig. 1 shows that at this temperature current carriers were just beginning to condense onto the impurities. At liquid nitrogen temperature (77°K) the impurity response was well marked out to 10 microns. At this temperature, Fig. 1 shows that the dark conductivity is some 6 orders of magnitude below the peak conductivity. On cooling the sample to liquid helium temperature (4°K), the impurity

response relative to the intrinsic response had increased and the impurity response band, at least on the long wavelength side, had sharpened.

The curves in Fig. 3 have been normalized to the intrinsic peak. Actually, correcting for mismatch of the series resistor, the $\Delta\sigma/\sigma$ at 4°K, 77°K, and 195°K, at the intrinsic peak were in the ratio $10^{-4.4}:10^{-0.8}:1$. However, as was evidenced by the "dark" currents measured with the sample at the low temperatures in the dewar used, there was considerable radiation illuminating the sample from background. The behavior in the intrinsic region at 4°K may be due to effects of this kind; the shift of the intrinsic threshold at the higher temperatures was well pronounced.

Because of large intrinsic response, this germanium sample was useful in determining if appreciable short wavelength scattering (below 2 microns) was occurring in the monochromator system: glass and quartz filters reduced the signal at long wavelengths to background signal when interposed between the source and entrace slit.

Because of the high sample resistance at low temperatures, the background signal during these measurements, although small, was apparently 60 cycle pick-up. No special effort was made to get down to the current noise level of the sample.

In Fig. 4 is shown the response of gold-doped germanium sample AA186. This sample was cut from the ingot adjacent to

sample AA178 and has a segmental cross section. The radiation was incident on the flat surface, the sample having a maximum thickness of about 130 mils. Reference to Figs. 3 and 4 shows that this thicker sample had a larger impurity response relative to the intrinsic peak. Fig. 4 also shows the relative change in response brought about by pumping on the liquid nitrogen coolant. The sharpening of the impurity band is evident.

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IV. Discussion of the Behavior of Gold Doped Germanium

The usual explanation of the thermal properties of germanium (and silicon and other semiconductors) doped with donor or acceptor type chemical impurities is made qualitatively in terms of a hydrogen model in which the attractive potential between the impurity ion and the bound charge carrier is reduced by a factor equal to the dielectric constant of the medium. The orbit radius of the bound carrier is m_oK/m times the electron orbit in the hydrogen atom (0.5 Å) and the ionization energy is m/m_oK^2 times that of the hydrogen atom (13.5 ev.); here m is the effective mass of the bound carrier and K is the dielectric constant.

Reasonable agreement is obtained with this model in the case of impurities in germanium such as arsenic or gallium, i.e., elements one periodic table column away from germanium. Taking K= 16.1 and m/m_o=0.2, the ionization energy is 0.01 ev., which is the average slope observed for such impurities in the conductivity versus inverse temperature curves. The orbit radius is about 40 Å which is large enough compared to the germanium lattice constant to lend support to the hydrogen-like model.

It must also be mentioned here that in attempting to fit experimental conductivity curves, for at least moderately doped germanium, one cannot obtain a good fit using a model consisting only of conduction band - discrete impurity levels

of one type (n or p) at one energy level - filled band. However, a good fit can be made if impurities or centers of opposite type are present. For example, to fit a curve for arsenic (n-type) doped germanium, one must include in the model the presence of almost the same order of magnitude of acceptors (electron traps). It is not known at present whether a good fit can be made using only one type of impurity if excited states are included.

Assuming the gold enters the germanium lattice substitutionally, only one of the four required valence bonds is fulfilled so that the gold impurity may be considered as a lithium-like acceptor impurity in the same sense as arsenic can be considered as a hydrogen-like donor impurity. There are three levels, therefore, to be considered. These are estimated to lie at 0.01, 0.05, 0.14 above the valence band. If the material has donor impurities in addition to the gold, electrons from these will be captured by the lower gold levels. This would account for the behavior of samples AA176 and AA177 with both lower levels filled and AA173 with only one gold level filled. This explanation is entirely hypothetical and further experimental and theoretical work is required to verify it or reveal an alternative explanation.

It might be pointed out that if gold enters the germanium lattice interstitially, it will give only a single level. However, the material would be n-type rather than p-type as the present samples are found experimentally to be.

V. Infrared Detector Using Gold Doped Germanium

As a preliminary test on the performance of these first gold doped cells as a practical detector at liquid nitrogen temperature, a simple optical system, dewar cell holder, and light chopper was set up.

The system employed the pyrex double dewar #2 with a 25 cycle metal blade chopper in front of the silver chloride window of the dewar. A 7" spherical mirror directed the radiation into the cell, and a germanium filter was interposed between the mirror and cell to eliminate short wave radiation.

With sample AA186 at 77°K, a hand or face at 25 feet gave a 20 db (or more) signal. Difficulty was experienced with radiation from the chopper as its temperature drifted above and below ambient temperature.

VI. Other Measurements on Germanium

The complete list of germanium samples measured during the period covered by this report is presented in Table I.

Table I

Germanium Samples Measured

Cell #	Crystal #	Added Impurity	ρ_{300°	Contact Type	Impurity Slope	$\frac{\Delta I}{V}$ at 4°K
AA86	210L	Quenched	3.5 ohm cm	Cu-plate	No well defined slope	3.0×10^{-2} uA/V
86	210L	Quenched	3.5 ohm cm	In	0.018 ev.	3.1×10^{-1}
104	240L	None	----	Cu-plate	0.048	4.0×10^{-3}
106	240L	None	----	Bi-Sn	0.045	3.8×10^{-2}
108	301L	None	----	Cu-plate	0.045	8.9×10^{-3}
109	301L	None	----	In	0.046	1.7×10^{-2}
120	310L	None	----	Cu-plate	0.044	1.7×10^{-2}
120	310L	None	----	In	0.046	2.6×10^{-3}
150	254A	As	8	In	0.012	7.2×10^{0}
154	227A	In	8	In	0.011	2.4×10^{-1}
171	343L	Zn	0.6	In	0.027	1.3×10^{0}
172	343L	Zn	0.2	In	0.027	3.4×10^{-2}
173	348A	Au	17.	In	0.050	3.7×10^{-3}
174	T258	Cu	12	In	0.047	1.2×10^{-2}
175	T258	Cu	6	In	0.047	1.0×10^{-2}
176	349A	Au	10	In	0.15	1.9×10^{-4}
177	349A	Au	10	In	0.15	9.3×10^{-5}
179	345L	Cu	2	In	0.046	1.1×10^{-2}
181	345L	Cu	0.6	In	0.046	4.2×10^{-2}

A. Contact Behavior

The group of cells AA86 through AA154 respectively in Table I were measured as part of the program concerned with the behavior of various types of contact to germanium. A discussion of the problem and previous results have been presented in the Twelfth Interim Report (N6onr23603).

Cell AA86, which was a piece of high purity germanium which had been thermally quenched from 830°C had been measured previously with copper-plate contacts. The cooling curve obtained (Fig. 5A) was anomalous in that, although the sample had low resistivity at room temperature, there was no rise in conductance near room temperature due to temperature dependence of mobility and that there was no well defined impurity slope. The same sample, when provided with indium contacts, behaved normally and gave the cooling curve illustrated in Fig. 5B.

Cells AA150 and AA154 were measured to complete the study of contact effects upon the behavior of germanium cells doped with impurities from Group III or V in the Periodic Table and to study the effect discussed in Section III(B) below. Both cells behaved normally. Thus far, no abnormal effects have been observed with doped germanium samples to which contact has been made with solders containing elements which can produce the opposite conductivity type. In other words, under the conditions

of preparation of the contacts, p-n or n-p junctions at the contacts appear not to be formed.

The group of cells AA104 to AA120 include high purity undoped germanium samples provided either with copper-plate or with modified contacts. In all cases, the behavior was normal. There were no significant differences which could be ascribed to effects at the contacts.

B. Low Temperature Dark Conductivity

Previously measured cooling curves for germanium cells generally showed a tailing off of "dark" conductance at temperatures of about 20°K or lower. This effect has been found, in most cases, to be due to tiny radiation leaks in the cell housing and cold shutter. When these leaks are eliminated, the dark conductance versus inverse absolute temperature curves decrease exponentially with no change in slope down to the point (conductance of 10^{-4} to 10^{-5} μA/volt) where electrical leakage interferes with the measurements.

C. Zinc Doped Germanium

A previous attempt to prepare zinc doped samples was unsuccessful because of the volatility of zinc at high temperatures. A subsequent modification of the doping technique resulted in the successful preparation of a crystal of low resistivity p-type zinc doped germanium. Two wafers, AA171 and AA172, cut from this crystal were measured in the Collins Cryostat. The

cooling curve for one of these samples is illustrated in Fig. 6. The other sample gave a similar curve. Zinc in germanium is of interest since it is an example of a helium-like impurity. The slope, 0.027 ev., observed in the intermediate temperature range is in agreement with the prediction of the behavior, on the assumption of a reasonable model, of this type of impurity. The much smaller slope exhibited at temperatures below about 20°K is not understood at present. It is not due to radiation leakage.

D. Copper Doped Germanium

The Group I b impurities, Cu, Ag and Au, are of particular interest since it appears that the largest impurity slopes for doped germanium will be obtained with lithium-like impurities of which these are examples. Gold doped germanium has been discussed in Section II.

Four copper doped wafers, AA174, 175, 179 and 181, cut from two different crystals and covering the room temperature resistivity range from 12 to 0.6 ohm cm have been measured. The cooling curve for AA175 is illustrated in Fig. 7. The behavior of the remaining samples was similar with a slight trend paralleling the room temperature resistivity values.

The temperature dependence of the impurity photoconductive response has been measured for this group of four cells with the results shown in Fig. 8A. The response in the neighborhood

of the maximum, at about 23°K, shows the regular dependence upon impurity concentration illustrated in Fig. 8B. Clearly, it would be desirable to investigate samples having an impurity concentration higher than that of AA181 in order to determine the concentration at which the photoresponse is maximal.

E. Measurements with NaCl Filter

In the study of the behavior of germanium to which various elements have been added as impurity, the cooling curves have shown slopes ranging from about 0.01 ev. to 0.15 ev. In the case of the largest slope, the photoconductive threshold has been found to agree with the thermal activation energy as determined from the cooling curves. In the other cases, limitations of our spectrometric equipment have prevented a similar comparison. From a practical point of view, it is the photoconductive response to that portion of the radiation lying below about 15 microns emitted by an object near ambient temperature rather than the response to the total radiation from such a source which is of primary interest.

Therefore, in one run in the Collins Cryostat, provision was made for interposing a rock salt filter at approximately the cell temperature in the path of the radiation from the top of the cryostat. With the cells at 4°K, the photoconductive response was measured with and without the filter in place. The results are presented in Table II. The expected photoconductive

Table II

Photoconductive Measurements with NaCl Filter

Cell No.	Impurity	Impurity Slope	λ_o -	$\frac{\Delta I}{\Delta I(NaCl)}$	$\frac{N_o}{N}$
AA150	As	0.012 ev.	103 μ	4.5	2.9
174	Cu	0.047	26	1.6	2.0
175	Cu	0.047	26	1.6	2.0
179	Cu	0.046	27	1.6	2.0
181	Cu	0.046	27	1.6	2.0
176	Au	0.15	8.3	1.5	
177	Au	0.15	8.3	1.3	

threshold λ_o has been calculated from the slope of the dark conductivity cooling curve. The ratio, $\Delta I/\Delta I(NaCl)$, is the observed ratio of the photocurrent with the rock salt filter removed to that with the filter in place and is uncorrected for reflection loss at the filter or for any possible change in the solid angle within which radiation is collected by the cells. There is seen to be a rough correlation between the threshold and the response ratio. For comparison, the ratio N_o/N which is the ratio for a black body at 300°K of the number of photons having wavelengths below the threshold to the number below 15 microns is included.

VII. Measurements upon Other Semiconductors

A. Zinc Oxide

A single crystal of impure zinc oxide had been measured some time ago and had been found to exhibit long wavelength impurity photoconductivity. When some samples of sintered zinc oxide became available, two of these, together with another single crystal for comparison, were measured in the Collins Cryostat. The cooling curves for the two sintered samples, one of which is illustrated in Fig. 9, were similar and showed two distinct impurity slopes. The single crystal sample gave a cooling curve similar to that previously observed (Fig. 16. Seventh Interim Report N6onr23603). The slope decreased continuously from about 0.01 ev. at about 70°K to a very small value at 4°K. The impurity photocurrents observed are summarized in Table III.

Table III

Zinc Oxide

Cell No.	Sample Type	Impurity Slope	$\frac{\Delta I}{V}$ at 4°K	$\frac{\Delta I}{I_D}$ at 4°K
AK33	Sintered	0.040, 0.0063 ev.	1.6×10^{-3} μA/V	0.23
AK34	Sintered	0.031, 0.0052	9.3×10^{-4}	0.21
AK37	Single Crystal	$\leq$ 0.013	9.5×10^{-3}	0.09

B. Cadmium Sulfide

One low resistivity cadmium sulfide crystal with indium contacts was measured in the Collins Cryostat. The cooling curve for this sample is given in Fig. 10. Although the conductivity at 4°K was about six orders of magnitude less than at room temperature and well defined impurity slopes were observed, no long wavelength photoconductivity large enough to be detected by a D.C. measurement could be detected.

C. Lead Sulfide and Lead Telluride

One single crystal sample each of lead sulfide and of lead telluride kindly provided by Dr. R. J. Cashman were measured to 4°K. For both, the conductance rose upon cooling from room temperature. Below about 20°K, the conductance was temperature independent. Both samples, apparently, are too impure to exhibit an impurity activation energy. The cooling curves obtained are presented in Fig. 11. No photoconductivity was observed.

D. Bismuth Iodide

Stoichiometric bismuth iodide has been found to be an intrinsic photoconductor with a threshold in the visible red. Several samples with deliberately added impurities, both excess iodine and metallic constituents, have been prepared and measured. Although there was evidence, both from determination of cooling curves and from photoconductivity measurements, for the successful

introduction of impurities, there was no reproducible evidence of any impurity having an activation energy of less than 0.6 - 0.7 ev.

E. Cuprous Iodide

Some preliminary measurements of the temperature dependence of conductivity of cuprous iodide have been made. The results thus far are not completely satisfactory because of contact difficulties; ionic conductivity and polarization in the neighborhood of room temperature and occasional cracking of samples upon cooling. A low resistivity sample containing excess iodine gave an impurity slope in the neighborhood of 0.01 - 0.02 ev. while a similar sample from which the excess iodine had been removed by a vacuum bake had much higher resistivity and showed a slope which gradually decreased from about 1.5 ev. near room temperature to about 0.2 ev. at about 160°K. If, as has been suggested in the literature, the impurity activation energy is concentration dependent, there is a possibility that a sample with an intermediate concentration of excess iodine will have useful photoconductive properties.

VIII. Recombination Radiation

Some mention was made of the breakdown which occurs in germanium at low temperature when a high voltage is applied to the specimen. It was felt that, under these conditions, the recombination rate as well as ionization rate would be high at impurity levels. If this is so, one might expect the generation of considerable long wavelength radiation. Tests were made on this in the Collins, with a sample having a 0.05 and 0.15 level as source, and as detector a sensitive germanium cell with an 0.01 ev. gap. No radiation could be detected under the conditions of test.

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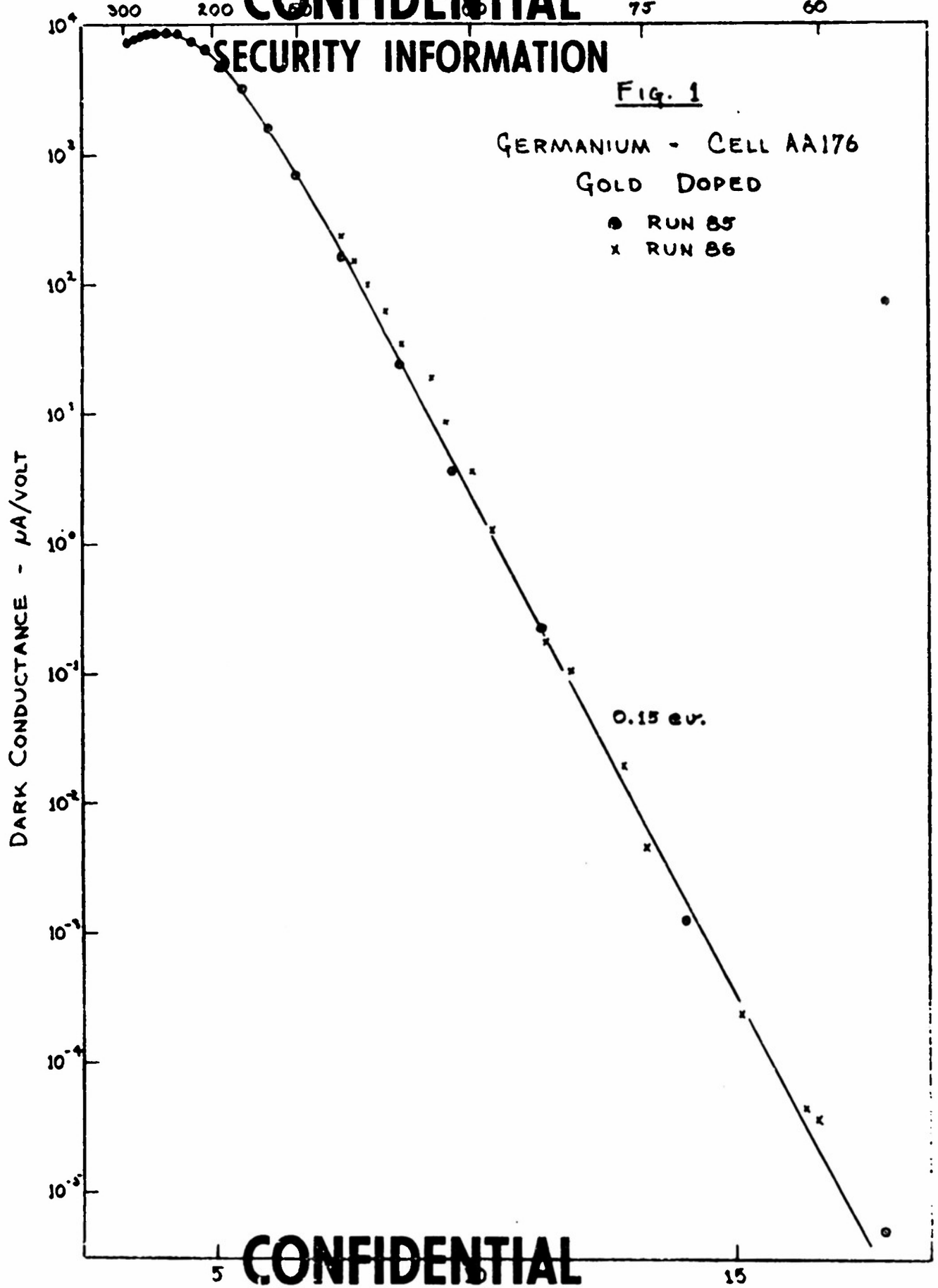
Fig. 1

GERMANIUM - CELL AA176
GOLD DOPED
● RUN 85
x RUN 86



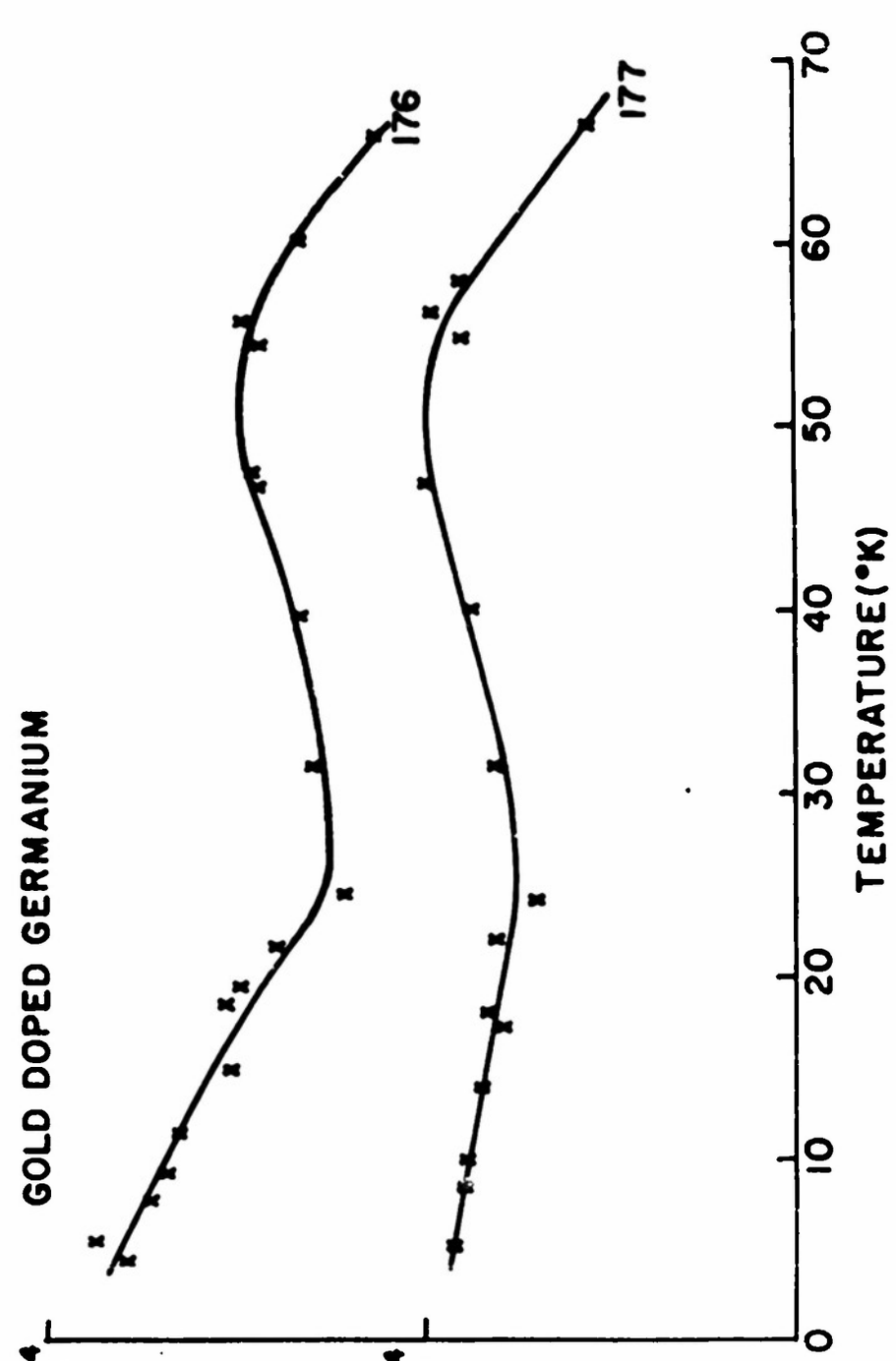
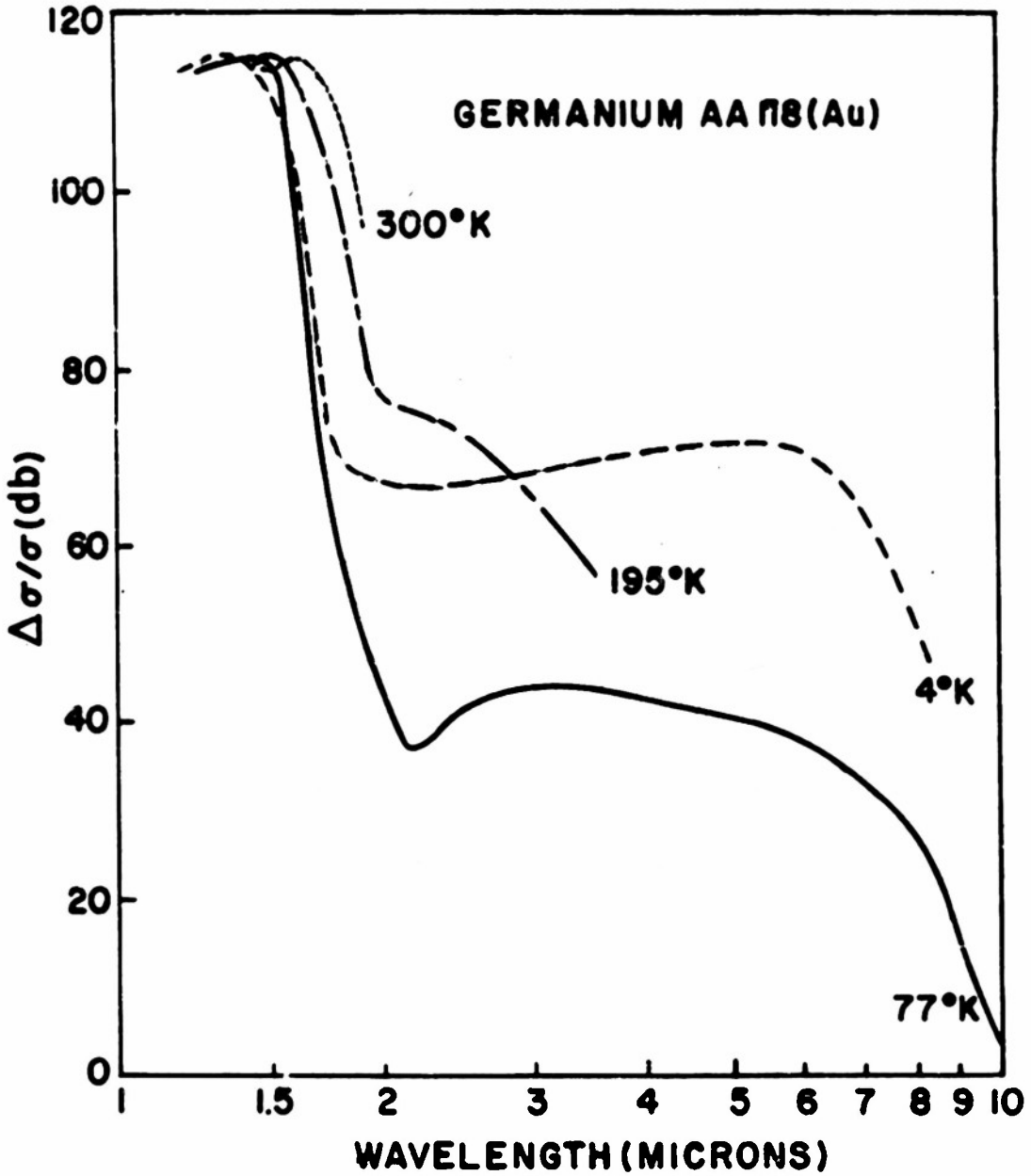


FIG. 2



SPECTRAL RESPONSE OF IMPURITY PHOTO CONDUCTIVITY OF GOLD-DOPED GERMANIUM

FIG. 3

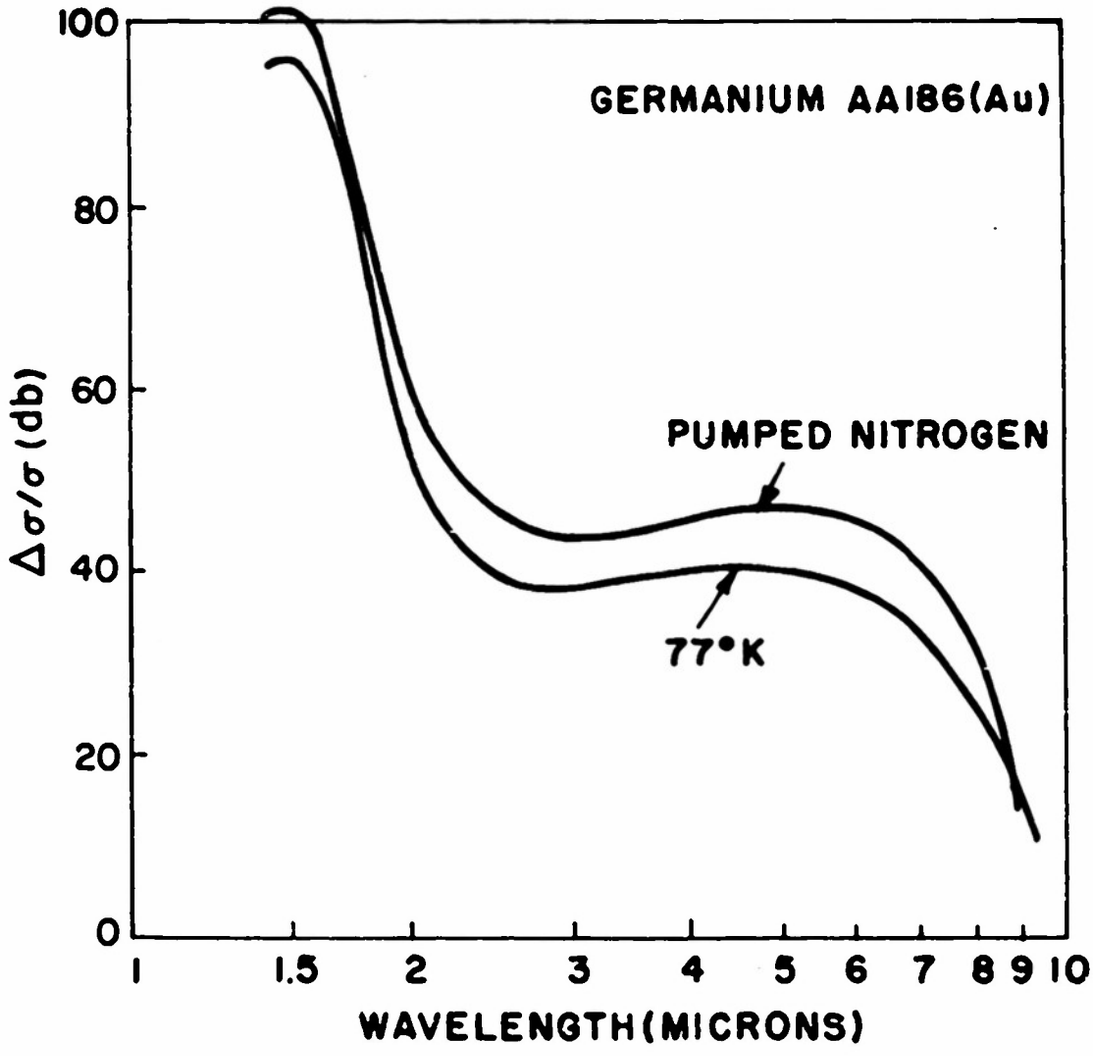

100
80
60
40
20
0
Δσ/σ (db)
GERMANIUM AA186(Au)
PUMPED NITROGEN
77°K
1
1.5
2
3
4
5
6
7
8
9
10
WAVELENGTH (MICRONS)

FIG. 4

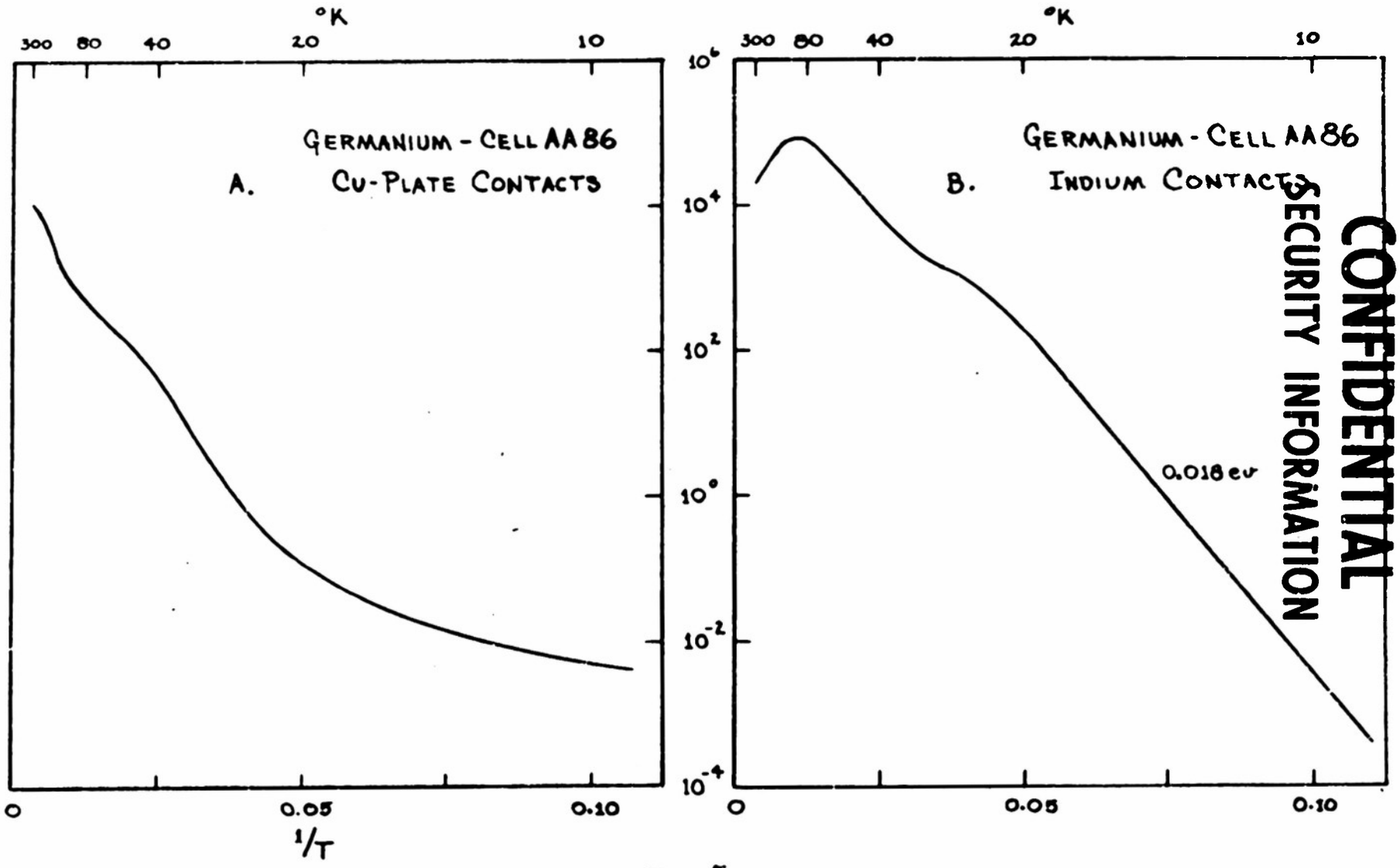


FIG. 5

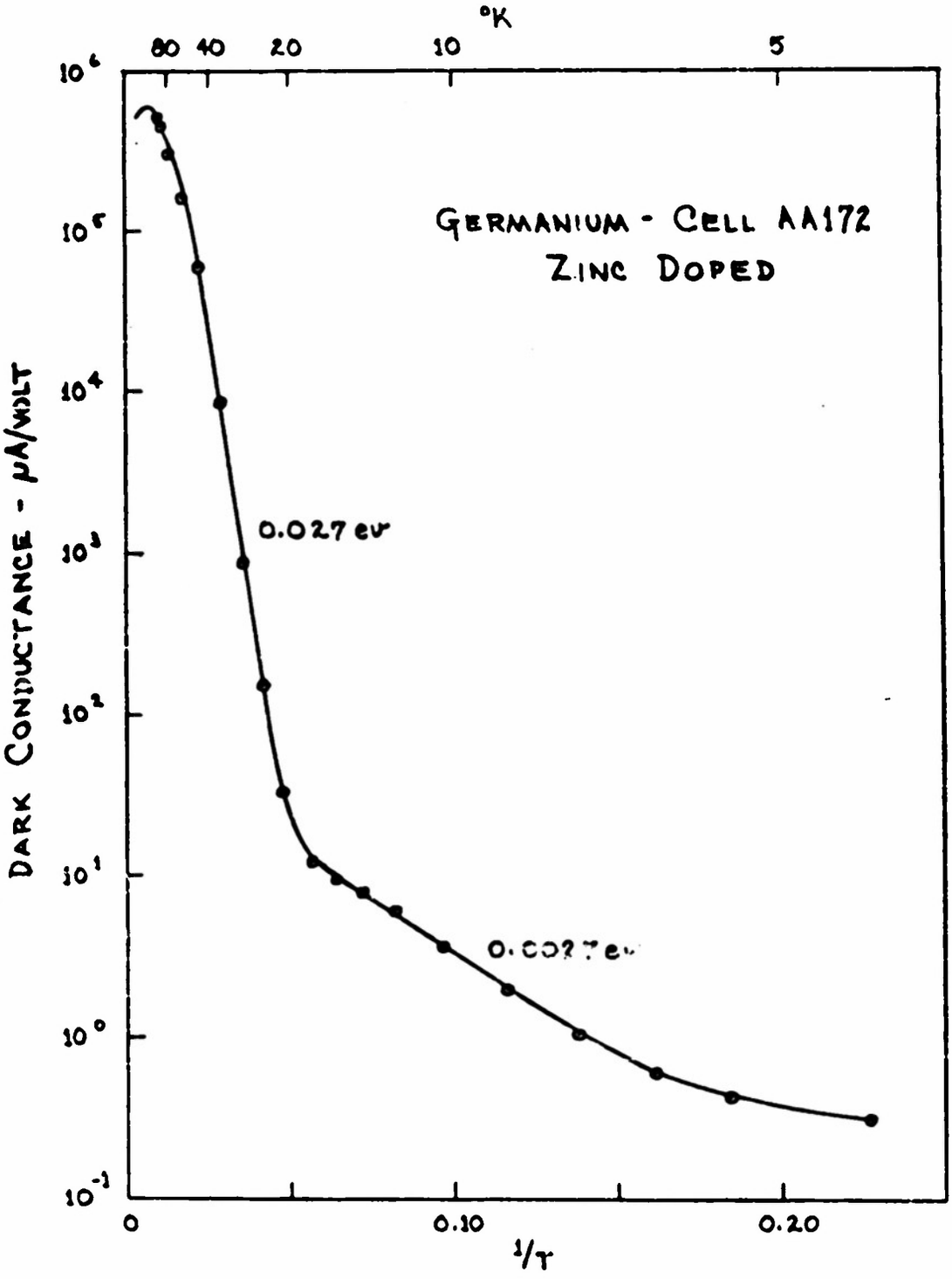

°K
80 40 20 10 5
GERMANIUM - CELL AA172
ZINC DOPED
0.027 ev
0.0027 ev
DARK CONDUCTANCE - μA/VOLT
10^6
10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
0
0.10
0.20
1/T

FIG. 6

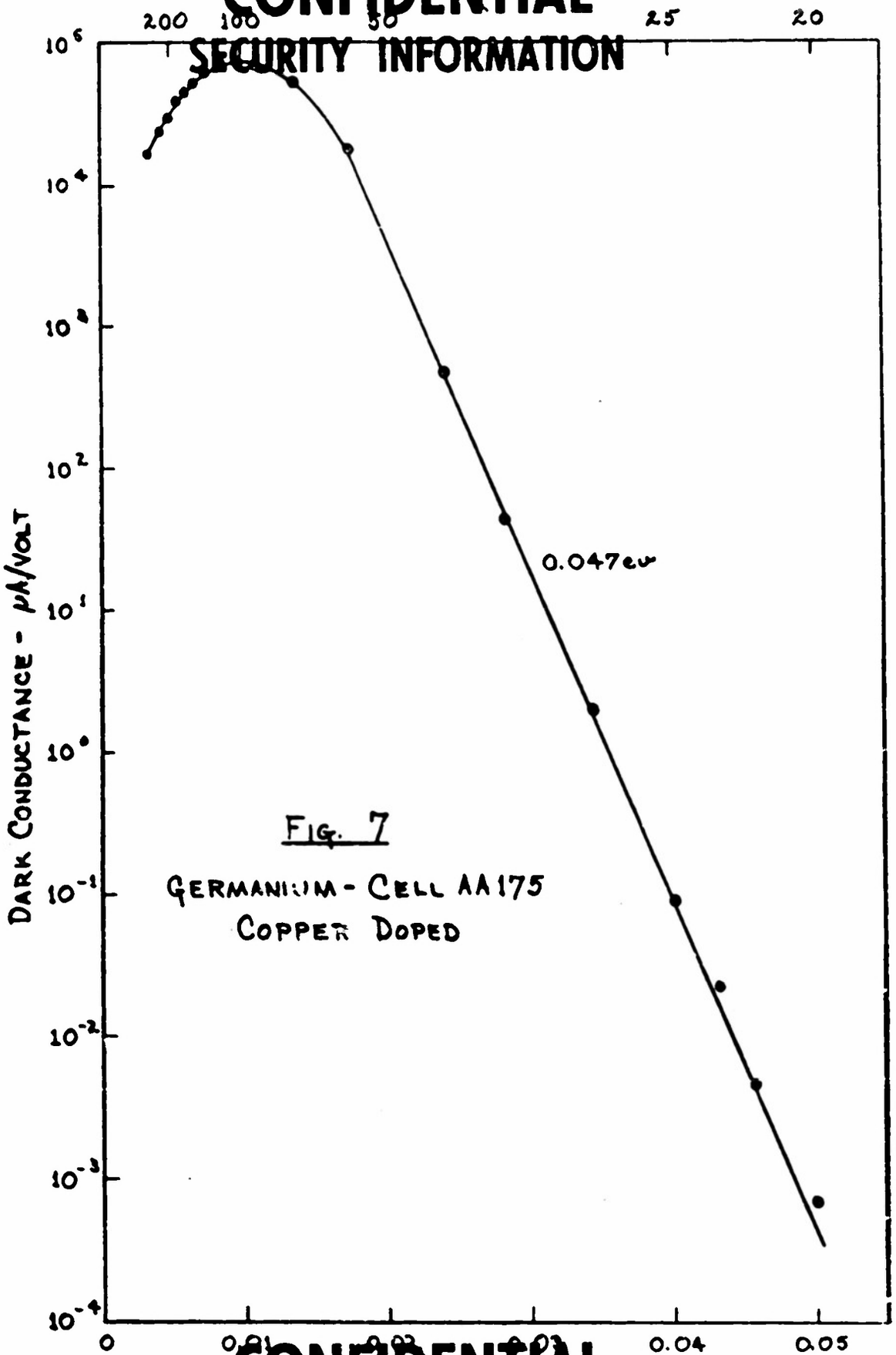


FIG. 7

GERMANIUM - CELL AA175
COPPER DOPED

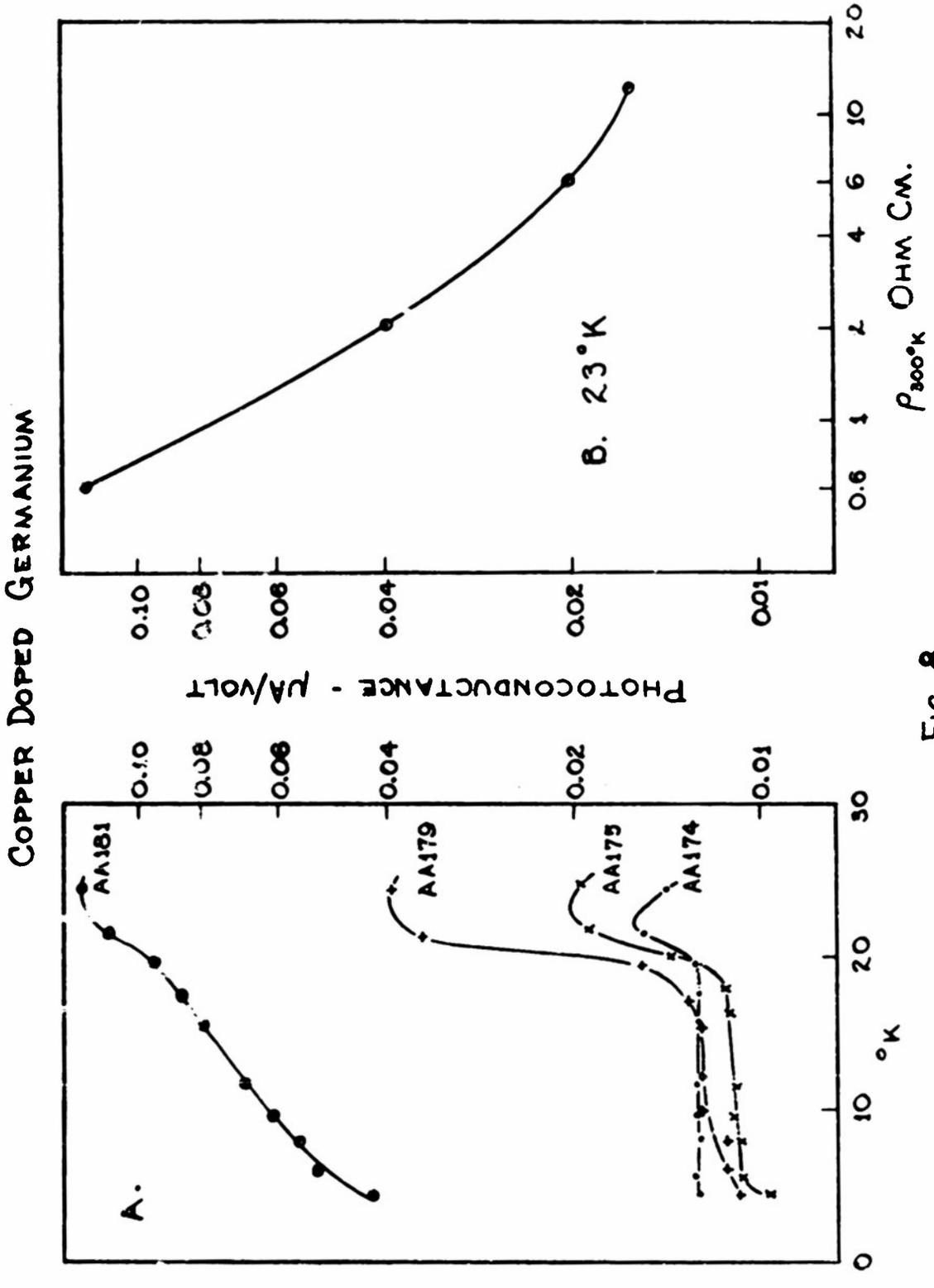


FIG. 8

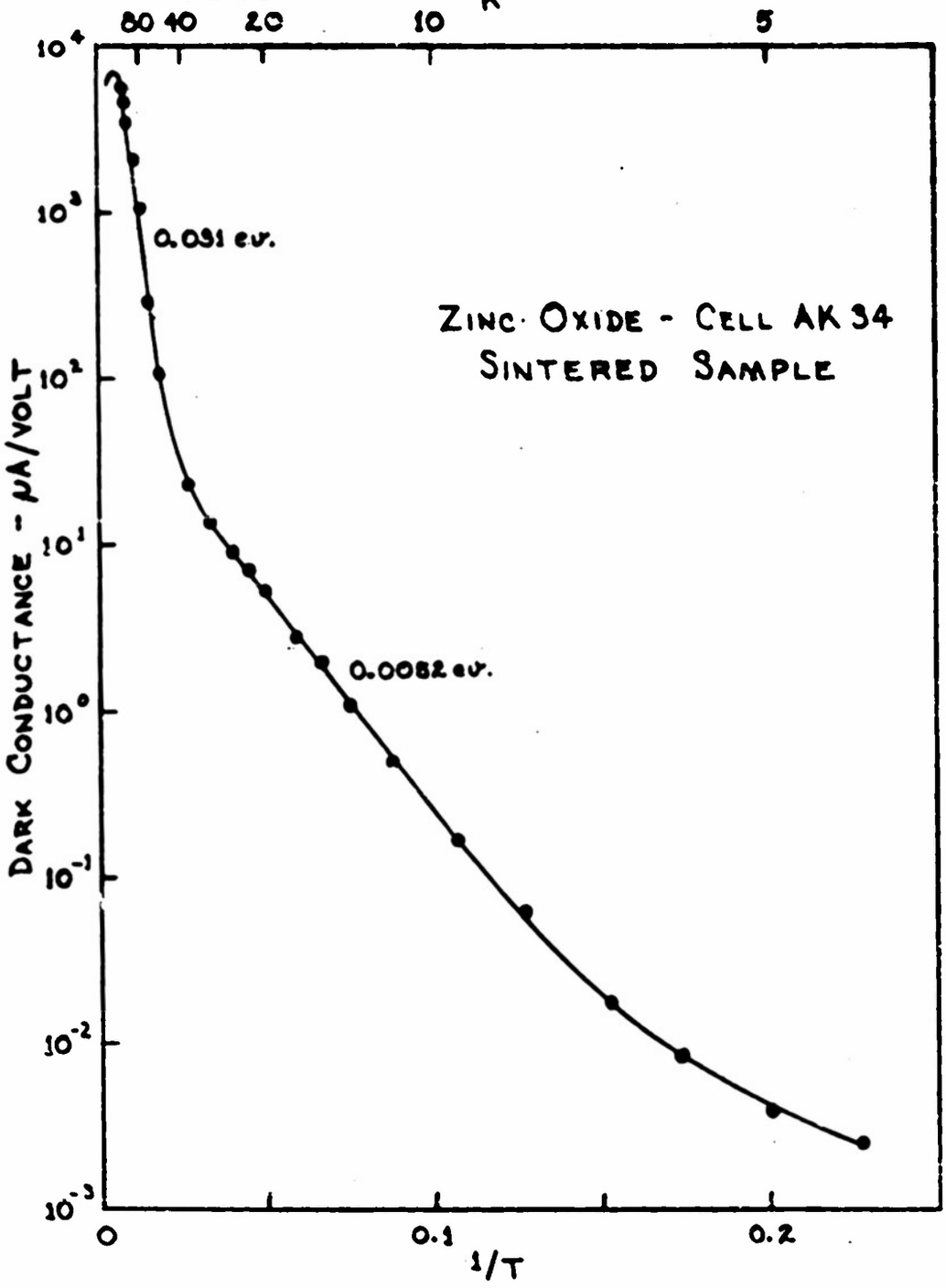

80 40 20 10 5
0.091 ev.
0.0082 ev.
ZINC OXIDE - CELL AK 34
SINTERED SAMPLE
DARK CONDUCTANCE - μA/VOLT
1/T
0
0.1
0.2

FIG. 9

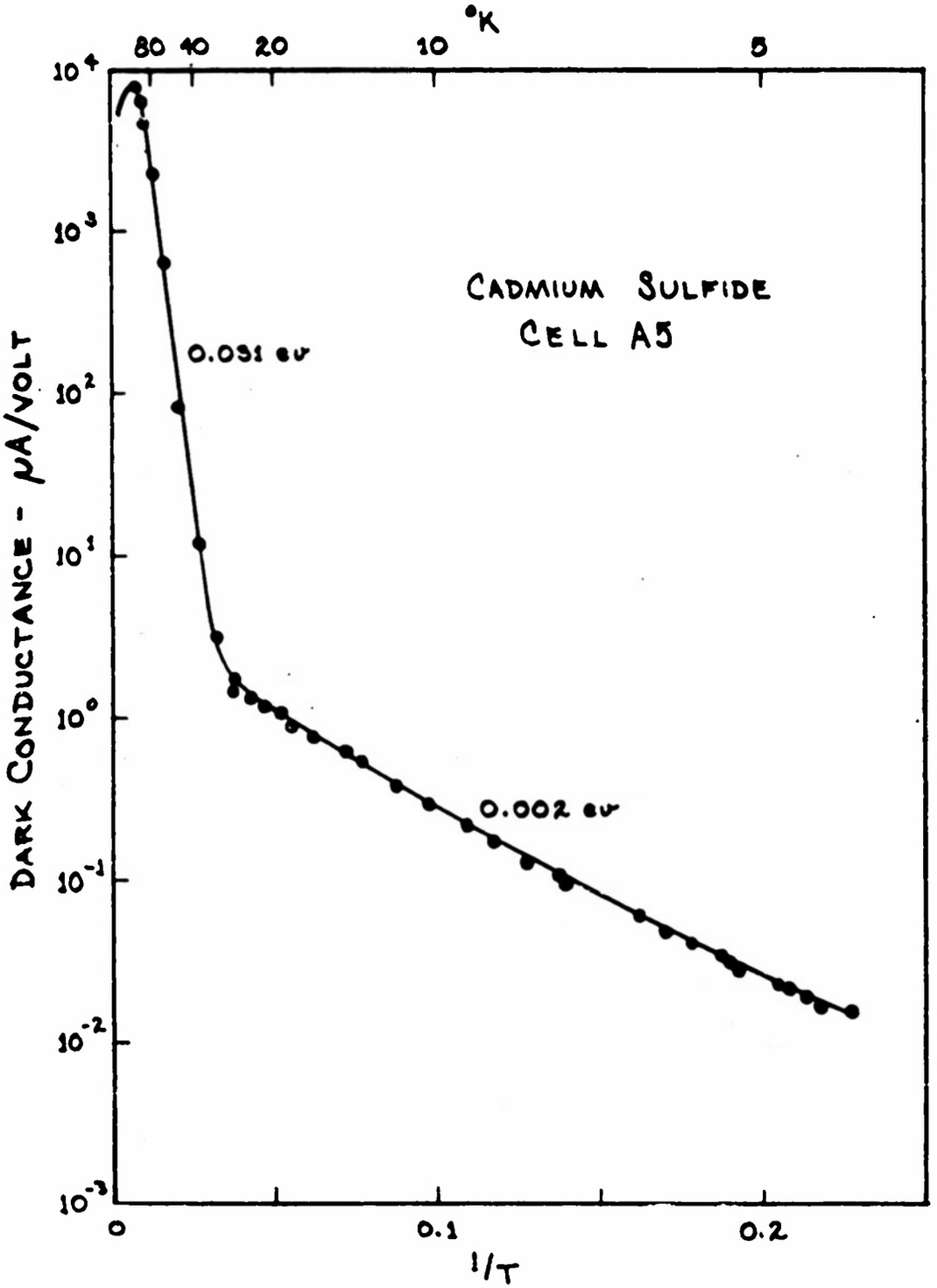
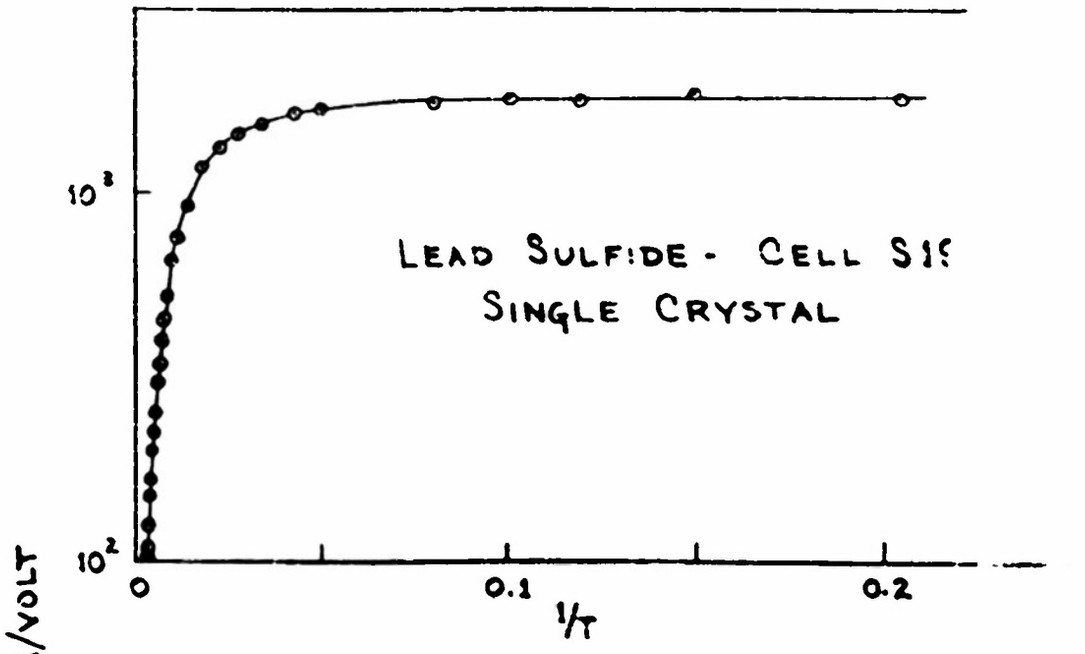
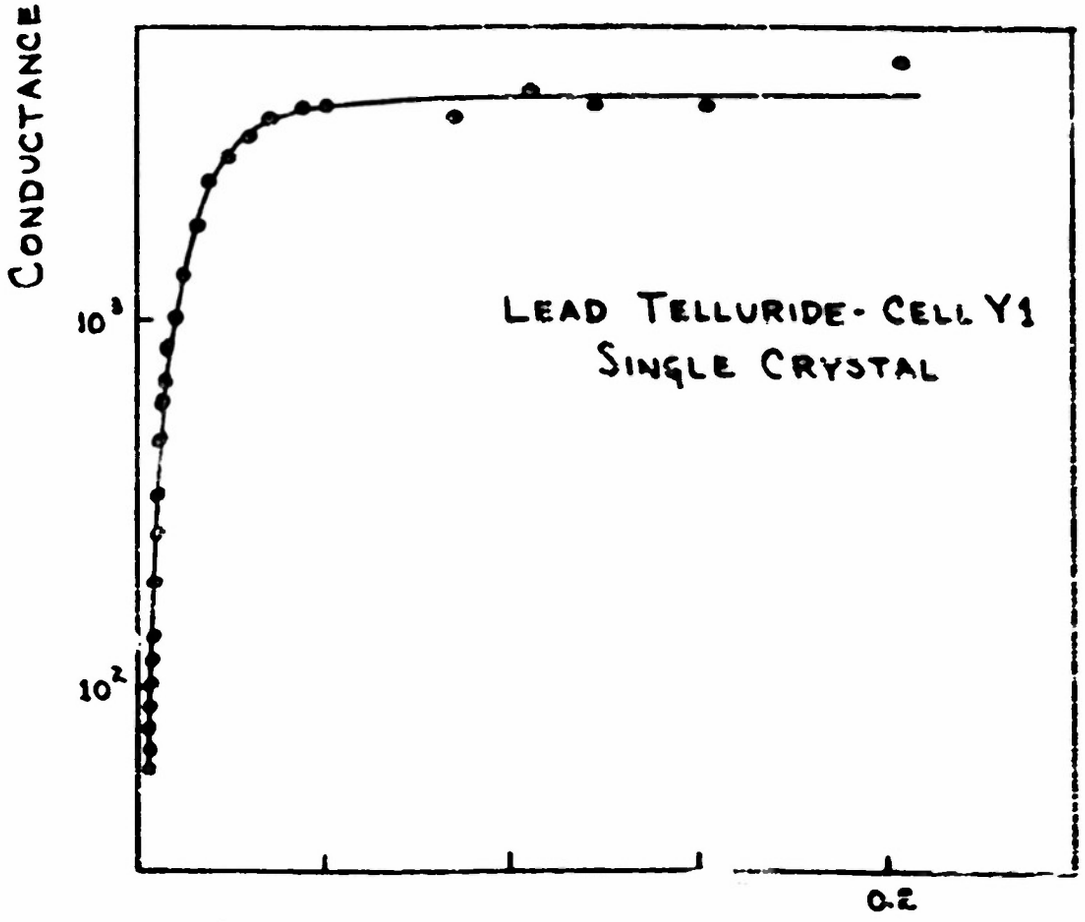


FIG. 10


LEAD SULFIDE - CELL S1
SINGLE CRYSTAL
10^3
10^2
0
0.1
0.2
1/T


CONDUCTANCE - A/VOLT
LEAD TELLURIDE - CELL Y1
SINGLE CRYSTAL
10^3
10^2
0.2